UNITED STATES ATOMIC ENERGY COMMISSION

AECD-3499

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October 24, 1952

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Technical Information Service, Oak Ridge, Tennessee

METALLURGY AND CERAMICS

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PRINTED IN USA
PRICE 10 CENTS
Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

Work performed under
Contract No. W-7405-eng-92.

Date Declassified: February 4, 1953

AEC, Oak Ridge, Tenn.-W31427

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ABSTRACT

The reclamation of machined zirconium chips by a process of washing, leaching, and pickling makes it possible to obtain material of low hardness.

INTRODUCTION

At the time of this study, these chips, if reclaimed and fed directly into an arc furnace, would have had a potential value of $35 per pound, but, if used as feed in the iodide process along with sponge, would have been worth only $15 per pound. Therefore, it was desirable to process the chips so as to make them suitable as feed for the arc furnace.

During machining, the chips are contaminated so that the ingots produced from them are excessively hard. Iron, carbon, silicon, and aluminum appear to be the elements picked up during machining.

EXPERIMENTAL WORK

PRODUCTION OF CHIPS

The zirconium chips used in this study were produced by milling and shaper operations. Soluble-oil coolant was used for milling operations. The shaping was done without a coolant.

The chips were classified according to the way in which they were formed—face-mill, straddle-mill, Sharon-Shaper, and Sharon-mill chips. The face- and straddle-mill chips were from the machining operations.

CONTAMINATION

Chemical analyses were made to determine the degree of contamination. The chip types and several sets of analyses which are indicative of the contaminants present are shown in Table 1. A typical analysis of WAPD iodide crystal-bar zirconium is included for comparison.

The analytical data show that the elements present in significantly larger amounts in the chips than in crystal bar are iron, aluminum, silicon, carbon, and oxygen. In two types of chips, considerable amounts of molybdenum were found and in one, a considerable amount of magnesium.

It is believed that the aluminum and silicon and possibly some of the iron come from dirt. The balance of the iron may come from wear of the tools. The carbon represents traces of the cutting fluid left on the chips; the oxygen comes from oxidation of the hot chip during machining. It is interesting to note that little nitrogen is picked up by the chips. This observation

TABLE 1. ANALYSES OF ZIRCONIUM CHIPS AND CRYSTAL BAR

Chip Type	Spectrographic Analyses (ppm)																				Chemical Analyses (ppm)		
	Fe	Al	Si	Ni	Sn	Zn	Cu	Mg	Mo	Mn	Cr	Pb	W	Ti	Hf	V	B	Be	Co	Ta	N	C	O_2
Sharon shaper	1100	310	170	80	<5	–	20	25	200	7	20	<10	<50	40	<300	–	1	1	6	<500	70	1300	–
Sharon mill	840	510	840	40	<5	–	40	25	175	4	10	<10	<50	40	<300	–	2	<1	<5	<500	20	1200	–
Straddle mill	1600	300	140	40	<10	<100	20	400	<10	<5	10	<10	<50	90	<300	<10	<1	<1	<5	<500	<20	700	1700
Face mill	700	700	80	5	<10	–	40	20	<10	5	<10	<10	<50	<10	<300	<10	2	<1	<5	–	30	1000	1000
WAPD crystal bar	300	20	50	30	<10	–	5	<10	<10	<10	30	<10	–	20	<400	–	–	–	–	–	20	200	–

agrees with published statements on the reaction of zirconium with air, namely, that reaction with oxygen occurs at lower temperatures than reaction with nitrogen.

Thus, it appeared that some of the contaminants of chips were mechanically held. This method of contamination would account for the carbon, aluminum, silicon and part of the iron. Another part of the iron and the oxygen would be contained in a surface film in the chip. The mechanically held contaminants could probably be removed by mechanical operations such as washing, scrubbing, and agitation. The second part would have to be removed by removing a part of the surface. Finally, the form of the chips would have to be altered before they would become useful arc-melting feed stock.

DECONTAMINATION PROCEDURES

Removal of Cutting Oils

Centrifuging was an effective method of removing the bulk of the cutting fluid. In the laboratory, this was done in a 14-inch basket at 3400 rpm for 15 minutes. The remaining oil is most effectively removed by solvent treatments. A one-half-hour washing in carbon tetrachloride and then in alcohol, followed by air drying, produced material with low carbon content, as shown in Table 2. As will be seen in Table 2, other cleaning techniques which were tried were not as effective.

Table 2. Effect of Cleaning Procedure on Carbon Content of Straddle-mill Chips

Cleaning Treatment	Carbon Content (ppm)
Centrifuged, washed with CCl_4 with agitation	200
Centrifuged, washed with Alconox with agitation	3400
Vapor degreased	2300
Soaked in hot nitric acid (30%)	700
Soaked in hot sodium hydroxide (20%)	800
Soaked in hot hydrochloric acid (20%)	900
WAPD crystal bar	200

Removal of Adhered Contaminants

Even after removal of the oil, the other mechanically held contaminants remain. Agitation of the chips on a screen was found to be effective in removing the bulk of the contamination. This was done in a gyratory riddle with openings of 0.017″ × 0.060″. Table 3 shows the effectiveness of this operation in removing contaminants. The effectiveness is also shown by the fact that some samples of the material passing through the screen contained as much as five per cent of iron.

Table 3. Analyses of Zirconium Chips Before and After Removal of Adhered Contaminants by Riddling

	Analyses (ppm)		
Chip Type	Fe	Al	Si
Straddle mill (before removal)	1600	300	140
Straddle mill (after removal)	190	20	60
Face mill (before removal)	700	700	80
Face mill (after removal)	520	<10	50

Although this procedure is effective in removing most of the adhered contaminants, sometimes iron oxide still adheres to the chip surface. Its presence can be detected by shaking the chips in dimethyl ether. Any iron oxide will give a definite red-brown suspension. The oxide can be removed by leaching in dilute hydrochloric acid (5 normal, 17-18 per cent) and washing.

Removal of Oxygen Contamination

The oxygen contamination is confined to a thin surface layer on the chips. Pickling appears to be the only feasible method for removing this layer. Since no pickling solution is known which dissolves the oxide and not the metal, it is necessary to remove some of the surface of the chip. The ZrO_2 layer is then "lifted" from the chip surface. A certain loss of metal naturally must be tolerated; this appears to be about 10 per cent.

The pickling solution used contained 50 volume per cent of 70 per cent nitric acid and water with an addition of one per cent of ammonium fluoride. Pickling was carried on for about eight minutes, using 1-½ gallons of pickling solution per pound of chips. The chips were agitated slightly during the pickling to promote more uniform attack. This operation removes about 12 to 15 per cent by weight of zirconium. The bath is replenished for further use by adding 0.20 pound of ammonium fluoride per pound of chips treated. After pickling, the chips are rinsed thoroughly with cold water, then rinsed in alcohol and dried.

Small ingots were melted from these chips. The hardness of the ingots was measured, since this was a more convenient method than an analysis for determining the oxygen removal. The data, given in Table 4, show that when 9 or more per cent of the chip weight was removed by pickling, ingots of low hardness were obtained. The hardness is higher than that of the original zirconium, but not much higher than if the sheet stock had been remelted without machining.

PREPARATION OF MELTING STOCK

Except for the straddle-mill chips, the chips used in this experimental study were a "hay-like" mass. In this form, they are useless as arcmelting feed stock, so, a few methods of preparing suitable arc-furnace feed were investigated.

The chips were subjected to several ball-milling tests using zirconium balls in a rubber-lined mill. This, however, was not satisfactory, since the grinding was not uniform, resulting in particles which ranged in size from fines, which formed a suspension with the alcohol used as a protective fluid, to masses which were unchanged.

An attempt was made to form solid charging stock by cold rolling 7″ × 1″ × ¼″ bars which were made by compaction of the chips under a tenton-per-square-inch pressure. This was unsuccessful, since the bar split during rolling before solid material could be produced. However, these cold-rolled bars, when nibbled, gave sand-like fines which were dense enough to pour easily. The bars which had been compacted only could also be nibbled into fines of quite high density. A disadvantage of this method, however, is that it subjects the chips to processes in which they could readily pick up contamination. It might be possible to decontaminate the chips after producing the fines, and, in this form, they could be briquetted or poured into tubes of zirconium foil.

ARC MELTING OF INGOTS

Almost all of the chips melted into ingots were prepared, after contamination removal, by compacting the chips in a ½-inch die. The slugs thus formed were used as feed stock for the arc furnace, and experimental ingots of 35 to 50 grams were usually melted.

Table 4. Results of Pickling Operations

Chip Type	Weight Loss, per cent	BHN* (3000 kg)
Straddle mill	8.6	115
	21.9	115
	24.7	117
	25.2	115
Face mill	6.1	164
	11.4	124
	22.2	115
Sharon shaper	6	108

* Hardness of ingots prepared from the treated chips was used as the criterion for oxygen removal.

To determine the more practical aspects of the reclamation procedure, uncompacted chips were used to melt a two-and-one-half-pound ingot and one eight-pound ingot. The hardness of these ingots, 170 and 129 Brinell, respectively, was considerably higher than that of the smaller ingots. Unfortunately, the melts became contaminated by the tungsten electrode and this is the most likely cause of the higher hardness. The tungsten contents were 1.2 per cent and 0.4 per cent, respectively.

The chips had a tendency to "float" against the electrode leading to their contamination. Proper arrangement of the gas inlet and feed tube, and shielding the electrode may avoid this contamination.

ANALYSIS

Complete data on materials cleaned as discussed in this report are given in Table 5.

Table 5. Analysis Limits and Result of Decontamination

	Analyses in ppm					
	O_2	N	C	Al	Fe	Si
Contamination limits	200	30	<400	80	550	100
Prior to cleaning and pickling	1700	20	3400	300	1600	140
After decontamination	200	20	200	20	350	60
For comparison: WAPD crystal bar		20	300	20	300	50

CONCLUSIONS

This study has shown that it is possible to remove most of the surface contamination of zirconium chips and produce a material with essentially the same composition as the material from which the chips were cut. Thus, it should be possible to use the chips in the same manner as heavier zirconium scrap, as melting stock.

If the material is to be remelted, some method of consolidating the long stringy chips into suitable melting stock will be required. A little work on this subject was done, and although no satisfactory method was developed, promising avenues of attack were found.

The study was terminated in favor of larger scale tests in chemical plants. For that reason, no detailed cost analysis of processing was made. However, it appears that costs should be reasonable, the largest being the 10-15 per cent metal loss in pickling.